

STUDIES OF COAL PRETREATMENT IN DIRECT LIQUEFACTION

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ABSTRACT

Studies have been done on pretreatment of three coals from the Argonne Sample bank (Zap Lignite, Wyodak subbituminous, and Illinois No. 6 bituminous). For each coal, samples of dried, ion-exchanged (using ammonium acetate), methylated, and demineralized (using HCl/HF) coal were prepared. The starting samples were characterized by several techniques (FT-IR, TG-FTIR, SEM/x-ray, FIMS, elemental analysis). Liquefaction experiments were done at 400°C (30 min) in dihydrophenanthrene (DPH). The two low rank coals that were modified by demineralization and methylation showed significant improvements in liquefaction yields, as indicated by the amounts of toluene solubles, oils, and pyridine solubles. The ion-exchange treatment was moderately beneficial for the Zap Lignite, and for the Wyodak, and had a modest negative effect on the Illinois No. 6. Drying the coal had a negative impact on the liquefaction yields for the two low rank coals, especially for the Zap Lignite, and little effect on the Illinois No. 6 coal. The trends for improved liquefaction yields were found to parallel trends for improved tar yields and lower CO₂ yields in a programmed pyrolysis treatment.

INTRODUCTION

Most of the proposed processing schemes for improving liquefaction yields involve overwhelming the retrograde reactions by simply enhancing the bond-breaking reactions. The retrograde reactions are often encountered before liquefaction temperatures are reached. Hence, it is important to focus on the retrograde reactions themselves.

The motivation of the present study comes from work that has been done on the pyrolysis of coals and modified coals. This work has identified several key factors which are important in retrograde reactions which occur under pyrolysis conditions. Solvent swelling (1,2) has been used as a method for measuring the crosslink density of pyrolysis chars. The amount of tar formation in pyrolysis is another indication of the amount of crosslinking which has occurred (3-7).

Measurements of the solvent swelling ratio for a number of coals pyrolyzed under the same conditions show that the early crosslinking, which reduces liquid yields, occurs in low rank coals (6-8). This result is consistent with the observation that the short time liquefaction yields are lowest for these coals (9). Suuberg et al. observed that the low temperature crosslinking associated with low rank coals appeared to correlate with the evolution of CO₂ (3,4). This correlation was confirmed in recent work done by Solomon and coworkers (6-8). The source of the CO₂ is presumed to be the carboxyl groups. Solomon et al. (8) found that the loss of carboxyl groups correlated well with the evolution of CO₂.

The water content of the coal also appears to play a role in retrograde reaction chemistry. Studies have shown that drying the coal can increase the amount of crosslinking which occurs in pyrolysis (5) and liquefaction (10). Similarly, steam pretreatment has been found to have a beneficial effect on pyrolysis (11) and liquefaction yields (12,13). Solomon et al. (8) also found a correlation between the loss in solvent swelling, the evolution of H₂O and the loss of hydroxyl groups.

In addition to solvent swelling and the tar yield, an examination of the tar molecular weight (MWD) distribution has been valuable in assessing the degree of crosslinking (7,14). It can be seen that the tar MWD measured by Field Ionization Mass Spectrometry (FIMS) for low rank coals drops off fairly dramatically above 200 AMU. The dramatic cut off is consistent with the occurrence of crosslinking in these coals and the lower tar yields that have been measured. When a low rank coal is

methyated, it has been found that the tar yield and the tar MWD begin to resemble a bituminous coal (14).

The removal of cations from a low rank coal by ion-exchange or demineralization also has a beneficial effect on the tar yield and the extent of crosslinking (15) in pyrolysis studies. The role of cations in direct liquefaction has not been extensively studied.

The results from these pyrolysis studies, which have shown the importance of oxygen functional groups, water content, and cations on crosslinking, provided much of the motivation for the present study of retrograde reactions in liquefaction using coals in which these concentrations have been modified.

EXPERIMENTAL

Coal Modifications - Three coals from the Argonne sample bank are being used (Illinois No. 6, Wyodak, and Beulah Zap). Coal samples have been prepared so that for each coal there is a supply of raw coal, dried coal, acid-demineralized coal, ion-exchanged coal for the removal of exchanged metal cations (Ca, Na, K) and methyated coal for the blocking of hydroxyl and/or carboxyl groups. All of the coal modifications were done at Advanced Fuel Research, Inc. (AFR), except for the methylation work which was done at SRI. The starting samples have been characterized by the following procedures: TG-FTIR to determine proximate analysis, condensable product yield, gas yields, etc.; elemental analysis to determine C,H,N,O, and S; mineral analysis and spatial distribution by a SEM/x-ray microanalyzer; quantitative FT-IR analysis of minerals and functional groups; FIMS analysis of molecular weight distributions of condensable products; and solvent swelling to determine the crosslink density.

Initial experiments on the methylation of coals using Liotta's (16) procedure were conducted with PSOC 1098, an Illinois No. 6 coal. Subsequent experiments were conducted with the Argonne Wyodak coal and the Argonne Beulah Zap Lignite.

Several techniques were used to assess the degree of alkylation. In contrast to literature reports, it was found that the titrimetric estimation of active hydrogens was very difficult because of the absence of clear end points. Infrared analysis (KBr Pellet, transmission mode) showed a distinct decrease in the % transmission in the OH region. However, the OH band was not eliminated. Elemental analysis of the methyated Illinois No. 6 coal showed that about 5 additional carbons were added for every 100 carbons. This result suggests that nearly all the hydroxyls were methyated.

Methyated Wyodak coal showed a very substantial decrease in the OH intensity, although the peak was not completely eliminated. The elemental analysis of the starting coal (dried) and the once methyated derivative gave the following compositions, assuming constant oxygen:

Starting Coal:	$C_{100}H_{72}O_{25}N_{1.4}$
Once Methyated:	$C_{116}H_{102}O_{25}N_{1.6}$

Every OH group that is methyated should result in an increase of one carbon and two hydrogen atoms. The observed increase in hydrogen [30] matches closely with that in carbon [16]. If the slight increase in nitrogen is to be ascribed to remaining tetrabutylammonium ions, the number of O-methyls introduced reduces from 16 to 12.

Methylation of the Argonne Zap lignite was also performed. The IR spectrum of the product showed a much larger amount of residual OH intensity as compared with the Wyodak. The extent of methylation was difficult to assess using elemental analysis.

Ion-exchanged samples of the three coals were prepared using a procedure similar to that used by Hengel and Walker (17). In this procedure, the alkali metal cations are removed by treatment with ammonium acetate solution. The coals were demineralized using the procedure of Bishop and Ward (18).

Coal Characterizations - Thus far, each of these three coals has been characterized by SEM/x-ray and TG-FTIR at AFR. The SEM/x-ray system is based on a method originally described by Solomon and Manzione (19). The results of the x-ray analysis of the ion-exchanged and demineralized samples confirmed that the concentrations of ion-exchangeable metal cations (Ca, Mg, Na, K) were significantly reduced in all three coals (20). For example, in the case of the Wyodak coal, the Ca content was 1.09, 0.11 and 0.04 wt.% for the raw, ion-exchanged, and demineralized samples, respectively. It was found that the Zap and the Wyodak coals have higher concentrations of Ca and Mg, which are often ion-exchanged on carboxyl groups in high oxygen coals. It was also noted that the demineralization process was much more effective at removing components of clays (Al,Si) than the ion-exchange procedure. The SEM analyses of the methylated coals have not yet been completed.

The results of TG-FTIR analysis of the raw, ion-exchanged, demineralized and methylated Zap lignite are shown in Figures 1 and 2. Each figure shows differential and integral plots for the major volatile species. An integral plot for the overall weight loss (labeled "Balance") is included as the first plot in each figure, along with the time-temperature profile and the sum of the gases measured by FT-IR (labeled "Sum"). The TG-FTIR analysis of the dried coal has not yet been done, although it should be noted that the standard analysis includes a short (~ 5 min) drying period at 150°C. The main differences are seen in the yield of tar, which has been identified previously (see Introduction) as a key indicator of the extent of crosslinking. The CO₂ yields were slightly lower for the demineralized and methylated Zap lignite when compared to the raw or ion-exchanged coal. The differences in the CO₂ (and CO and H₂O) yields are primarily in the shape of the evolution profile rather than the overall yield. An early CO₂ feature that was present for the raw and ion-exchanged Zap lignite was absent in the demineralization and methylated samples. The corresponding tar yields are higher for the latter coals. From these results, one can infer that the amount of crosslinking decreases in the order methylated < demineralized < ion-exchanged < raw. The results for the Wyodak coal were very similar. However, the results for the Illinois coal were not significantly different for the various pretreatments when compared to the raw coal (20).

Pyrolysis-FIMS analyses were done of the raw coals and modified coals. The spectra of the demineralized and methylated low rank coals more closely resemble the spectra of bituminous coals, which is consistent with a reduction in low temperature crosslinking, as discussed in the Introduction. The Py-FIMS results for the Zap lignite and Illinois No. 6 coal are shown in Figures 3 and 4, respectively.

Liquefaction Experiments - After the samples were characterized, experiments were done under coal liquefaction conditions in a microautoclave reactor which allows for gas analysis (20). The experiments were done in dihydrophenanthrene (DPH) at 400°C for a period of 30 min. The yields of toluene solubles, pyridine solubles, residue, and gas were determined (20).

RESULTS

The results of liquefaction experiments with the coals and modified coals are summarized for the Zap lignite and Illinois No. 6 bituminous coals, respectively, in Figures 5 and 6. The oils are classified as toluene soluble and hexane soluble. The results for the Wyodak subbituminous coal (not shown) are similar to those for the Zap lignite (20). The results show that the decrease in crosslinking, as implied by the reduction in CO₂ yield, roughly correlates with the increased liquefaction yields based on the toluene solubles. The trends in CO₂ yield and toluene solubles from liquefaction generally parallel the results for CO₂ yield and tar yield, respectively, determined from pyrolysis in the TG-FTIR analysis. However, the differences in total CO₂ yield observed in the liquefaction experiments are more dramatic than those observed in the pyrolysis experiments.

The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal. Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange procedure had a modest negative impact. In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.

In the case of methylation, a similar beneficial result has recently been observed by Miller et al. (21) in liquefaction studies with the Argonne Wyodak coal. The suggested explanations were a reduction in hydrogen bonding in the coal and a possible reduction in crosslinking reactions involving OH groups. A contributing factor may be the introduction of additional donatable hydrogen into the coal which allows stabilization of reactive fragments before they can crosslink.

CONCLUSIONS

The preliminary conclusions from this study are as follows:

- The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal.
- Ion-exchange has a modest positive impact for most low rank coals while drying has a modest negative impact. Drying had little impact on the liquefaction yields from the bituminous coal, while the ion-exchange treatment had a modest negative impact.
- In nearly all cases, the changes in the amounts of pyridine solubles by these pretreatments parallel the changes in the amounts of toluene solubles.
- The results from pyrolysis studies of crosslinking in coals and coals modified by methylation, demineralization, or ion-exchange are relevant in liquefaction.

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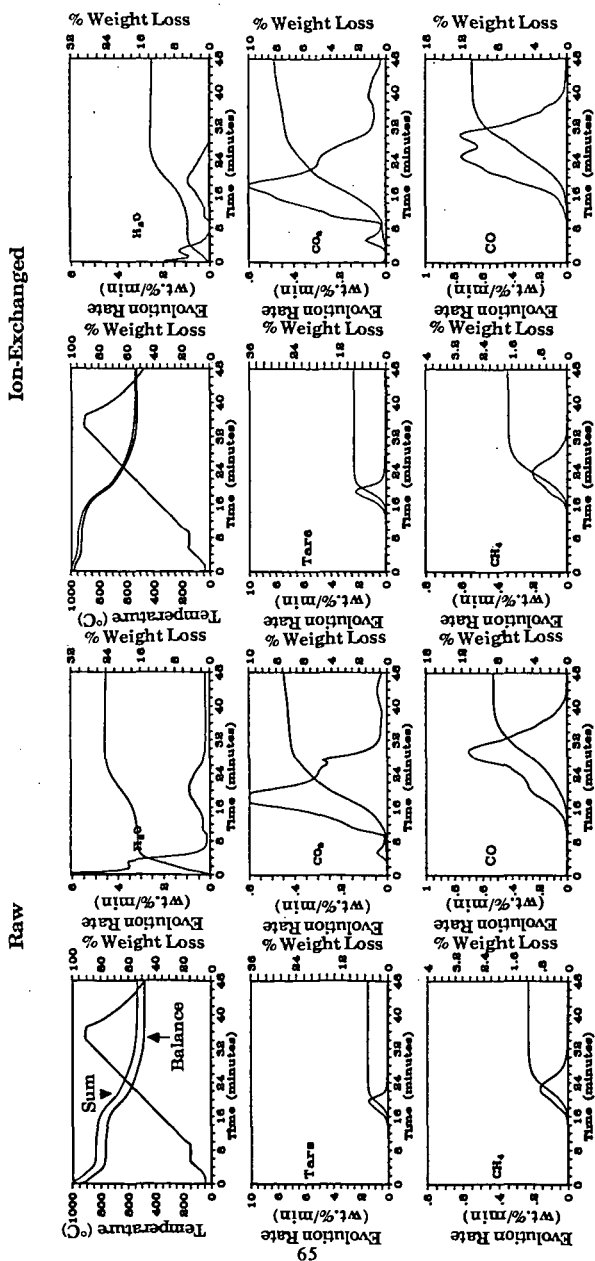


Figure 1. TG-FTIR Analysis of Zap Lignite.

Demineralized

Methylated

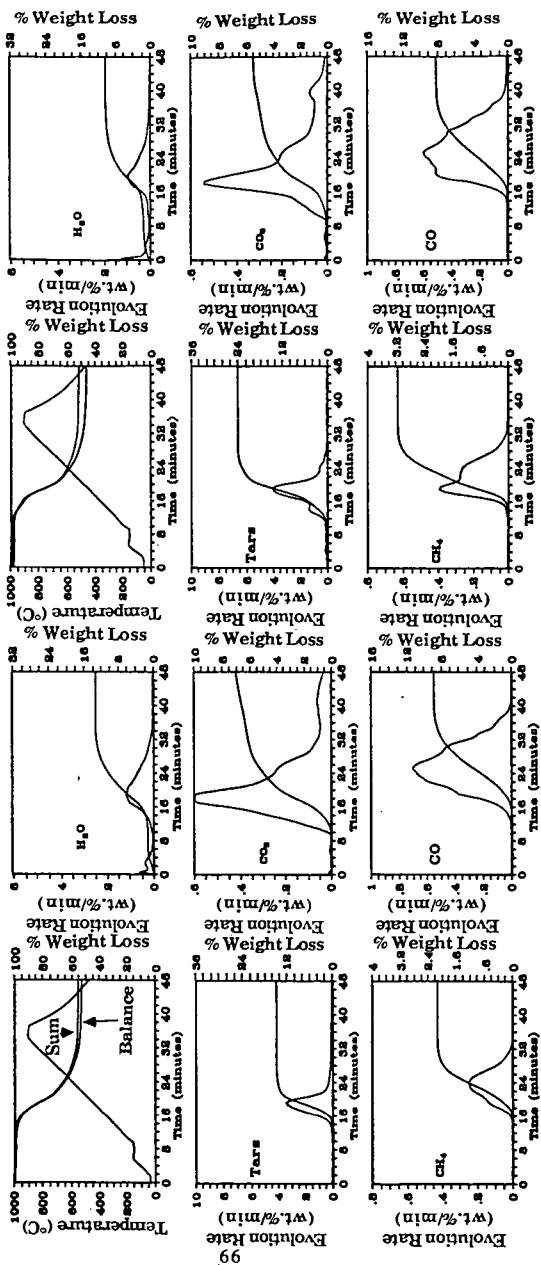


Figure 2. TG-FTIR Analysis of Zap Lignite.

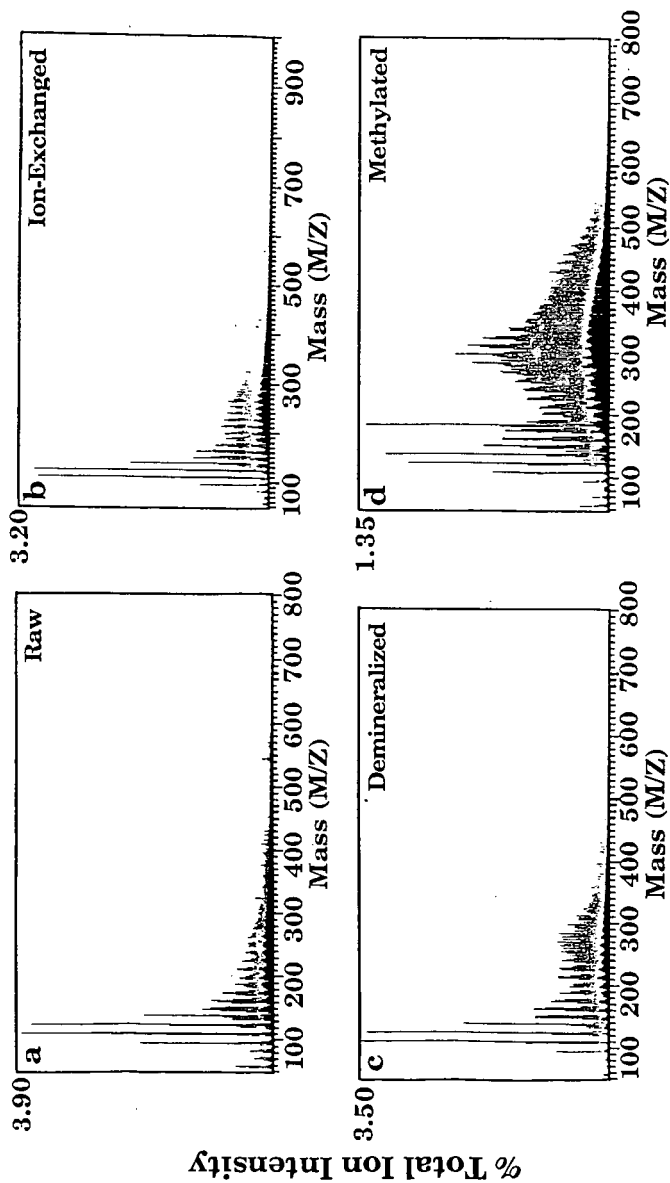


Figure 3. FTMS Analysis of Zap Lignite.

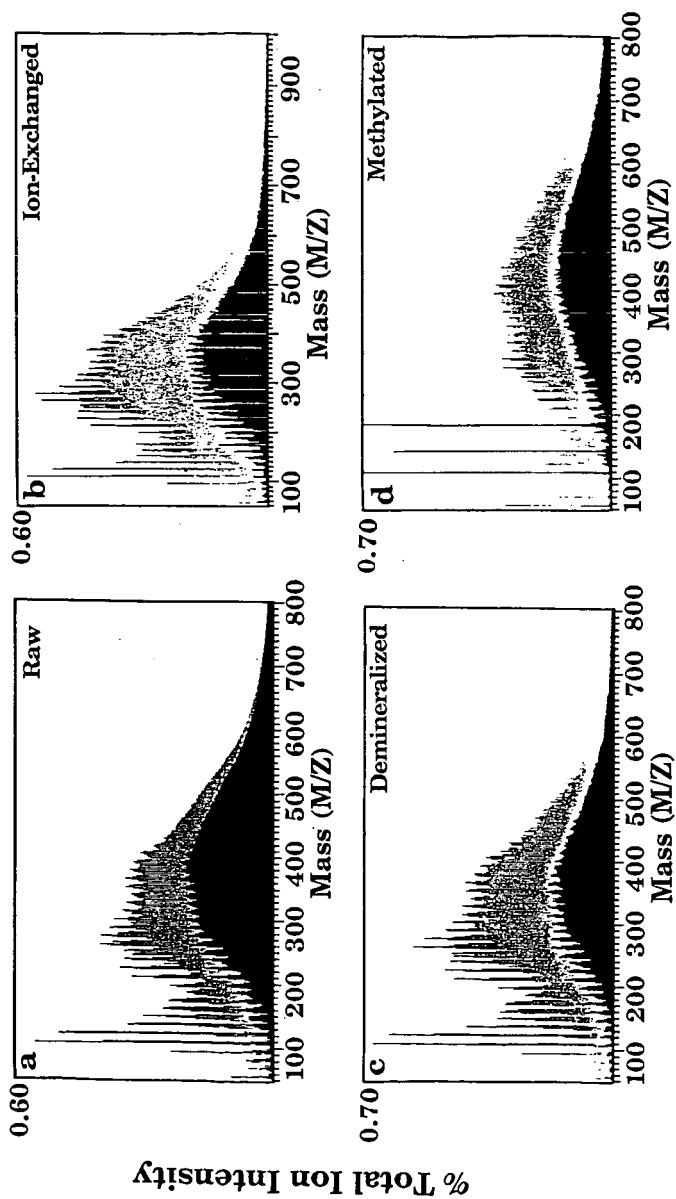


Figure 4. FIMS Analysis of Illinois #6.

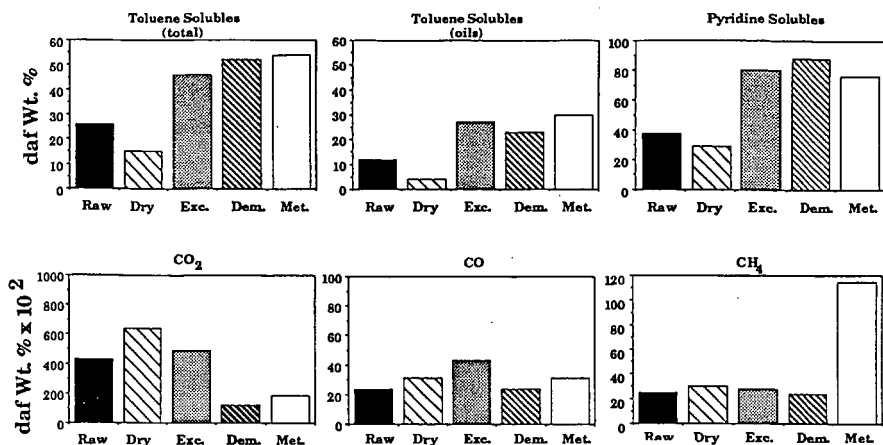


Figure 5. Liquefaction Results for Zap Lignite.

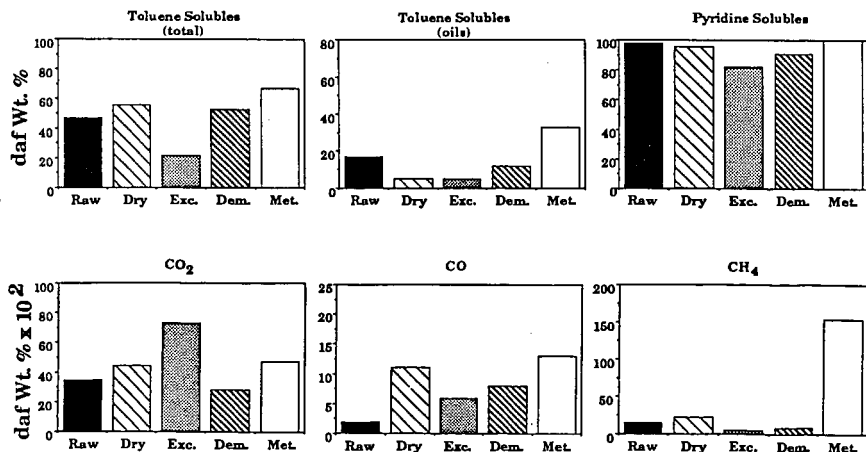


Figure 6. Liquefaction Results for Illinois #6.